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Effect of thermal treatment conditions on the properties of onion-like-carbon based polymer composite

J. Macutkevicius^{1*}, D. Seliuta¹, G. Valusis¹, J. Banys², S. Hens³, V. Borjanovic³, V. Kuznetsov⁴,
O. Shenderova³

¹ Centre of Physical and Technological Sciences, Semiconductor Physics Institute, A. Gostauto g. 11, LT-01108 Vilnius, Lithuania, Phone: +370 5 212 4539, Fax: +370 5 262 71 23. E-mail: jan@pfi.lt

² University of Vilnius, Sauletekio al. 9, LT-00122 Vilnius, Lithuania, tel. +370-5-2687015, Fax: +370-5-2687009, E-mail: juras.banys@ff.vu.lt;

³ International Technology Center, Raleigh, NC 27715, USA, Phone: +1 (919)-881-0250(-226), Fax: +1 (919)-881-0440, E-mail: oshenderova@itc-inc.org

⁴ Boreskov Institute of Catalysis SB RAS, Lavrentiev Ave. 5, Novosibirsk, 630090, Russia, Phone: +7-3833-308765, Fax: +7-3833-308056, E-mail: kuznet@catalysis.nsk.su

ABSTRACT

Dielectric properties of onion like carbon (OLC) and polyurethane composite prepared using different procedures were investigated in the frequency range up to 1 MHz. We show that broadband dielectric spectroscopy is powerful tool to determine technological fingerprints in the studied materials. It is demonstrated that cured samples annealed at temperature close to the melting point (450 K) exhibit substantially higher dielectric permittivity and electrical conductivity in comparison with untreated samples. With the increase of temperature of an untreated sample, its dielectric permittivity, electric conductivity and critical frequency increase, while Maxwell-Wagner mean relaxation time and aggregate sizes of OLC decreases. Annealing of the composite at temperature close to the melting temperature produce sample with more homogeneous distribution of OLC. The temperature dependence of conductivity of the homogeneous sample is mainly caused by a weak positive temperature coefficient effect.

Keywords A. Nano composites, B. Transport properties, E. Annealing, E. Heat treatment, Onion-like Carbon.

1. Introduction

Electrically percolative polymer-based composites have been attracting much attention because of their potential applications such as electroactive materials, sensitive materials, and electromagnetic coatings. Owing to the advanced electrical, thermal, and mechanical properties, various carbon nanoparticles like carbon nanotubes or carbon black have been widely studied and often used as nanofillers in the past few years. The main advantage of carbon nanotubes versus other carbon nanofillers is their extremely low percolation threshold [1]. Nevertheless, the percolation threshold in carbon nanotubes based composites depends on many factors such as polymer type and dispersion method [2]. The onion-like carbons (OLCs), consisting of stable defected multishell fullerenes, exhibit high conductivity similar to carbon nanotubes [3]. The OLC have a rare structure allowing for hierarchical assembly of conductive structural units and high concentration of electrically active defects, being able to absorb a wideband of electromagnetic radiation [4].

* Corresponding author. Fax: +370 5 262 71 23. E-mail address: jan@pfi.lt

Nevertheless, the first investigations of OLC based composites have shown low dielectric permittivity and electrical conductivity similar to the pure polymer matrix parameters [5-7]. It was observed, however, that the dielectric permittivity and electrical conductivity drastically increase in onion-like-based composite approaching the percolation point [8]. It is interesting to note that in the OLC polyurethane (PU) composite, the percolation point of a 10% volume fraction is estimated [8], and this is lower than a prediction from an effective medium approximation for the inclusions with a spherical shape (the percolation threshold for spherical inclusions is close to 1/3 volume fraction [9]). Carbon black topology is similar to OLC. For carbon black, the percolation threshold depends on the preparation technology and can be similar to carbon nanotubes, i.e., it can be also very low [10]. Therefore, for OLC applications it is very important to find optimal technological ways to further reduce the percolation threshold [8] and to study the effect of technological procedures on the electrical/dielectrical properties of the structures.

In this paper, we therefore, investigate an influence of preparation conditions on OLC/PU dielectric properties in order to find a most favorable technology for producing coatings with a low percolation threshold. In more detail, we explore the role of heating of the samples during mixing of OLC and PU solution as well as annealing effect of the cured films.

2. Sample preparation technology and experimental part

The OLC material was produced by annealing of detonation nanodiamond powder in vacuum at 1800 K, as it described by Kuznetsov *et al.* [3]. Nanodiamonds were purchased from New Technologies, Chelyabinsk. Average primary particle size of DND was 4 nm and the average volumetric aggregate size was 120 nm. To achieve fully transformed DND into OLC, DNDs were heated in vacuum 10^{-4} torr at 1800 K for 2 h. Size of primary OLC particles is around 6–7 nm, while average aggregate size is 130 nm for OLC dispersed in *N*-methylpyrrolidone solvent as measured by dynamic light scattering technique.

Samples of OLC were mixed with commercial formulation of oil-based polyurethane "Minwax clear satin" containing 60% of volatile compounds. All samples contained 15wt.% of OLC. Six samples were prepared under different thermal treatment conditions (more detailed information can be found in Table 1). First, after manual mixing with the OLC powder, the polymer suspension was magnetically stirred at 400 rpm during 24 hrs at 50 °C. Then, before casting a suspension, samples 2 and 3 were additionally heated at 70 °C and 90 °C, correspondingly, on a hot plate with a purpose to improve uniformity in distribution of OLC in a polymer solution with a lower viscosity. Then suspensions were casted on a Teflon substrate and dried at ambient conditions at 45 °C overnight. Half of the dried samples ("b" series) were additionally annealed at 150 °C during 1 hr under pressure in an oven. A motivation for this treatment originated from our observation that after testing of dielectric properties of the samples at high temperatures (for example, 450 K), dielectric constants and conductivities of the samples, when cooled to the room temperature, were increased. Thus, we introduced an annealing stage during sample preparation. Thickness of OLC/PU films varied between 250 and 700 μm . Distribution of OLC in PU matrix was characterized by scanning electron microscope SEM Zeiss Supra 25.

To characterize the samples we have employed broadband dielectric spectroscopy. This technique was already proved to be powerful tool to characterize these materials [5, 6, 8]. The complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$ was measured by a capacitance bridge HP4284A in the frequency range 20 Hz–1 MHz. Measurements have been performed on cooling and heating at a rate of about 0.5 K/min. Each measurement started from heating, and after reaching 450 K, the sample was kept at this temperature for ~0.5hr, and then the samples were cooled down to room temperature.

3. Results and discussion

Figure 1 illustrates SEM images of the top view of the samples 3a and 3b at the same magnification. As can be seen from the images, OLCs are uniformly distributed within the matrix and OLC aggregate sizes are smaller in the annealed sample 3b.

The frequency dependence of dielectric permittivity ϵ' and electrical conductivity σ' at room temperature for composites prepared under different conditions with OLC concentration of 15% is shown in Fig. 2. It can be seen that both dielectric permittivity ϵ' and electrical conductivity σ' is strongly influenced by preparation conditions. In particular, it is more pronounced at low frequencies. All annealed samples (1 b–3 b) exhibit higher electrical conductivity σ' and dielectric permittivity ϵ' in comparison with not treated samples in the frequency range up to 1 MHz. The highest electrical conductivity σ' and dielectric permittivity ϵ' are observed in 3b sample. The increasing of dielectric permittivity ϵ' at low frequencies (below 300 Hz) in the annealed sample is obviously caused by Maxwell-Wagner relaxation [11]. In order to explain an effect of annealing on the dielectric properties, measurements of dielectric properties were performed under heating at different frequencies. These results for the most representative samples 3a (not annealed) and 3b (annealed) are shown in Fig. 3. As one can see, the dielectric permittivity ϵ' and electrical conductivity σ' increase on heating in both annealed and untreated samples, however, in the untreated sample the increase is more pronounced. It is worth noting that more pronounced changes of dielectric properties take place at low frequencies. The electrical conductivity also exhibits a kink in sample 3b at nearly 380 K. It is probably associated with the fact that polymer molecules can move more freely at this temperature, because conductivity and dielectric permittivity of pure polyurethane also exhibit kinks close to this temperature. Usually, such temperature is associated with alfa (glass) transition in polymers [12]. To get deeper insight into processes, frequency dependence of dielectric permittivity ϵ' and electrical conductivity σ' on the heating of composites 3a and 3b are plotted and presented in Fig. 4a and Fig. 4b, respectively. It can be seen that the dielectric permittivity ϵ' measured at room temperature strongly decreases with the frequency, meanwhile electrical conductivity strongly increases with frequency in the untreated sample. Thus, it is not possible to estimate DC conductivity in our frequency range. On further heating of untreated sample frequency-independent (DC) conductivity becomes observable only at low frequencies.

To analyze the data, we have used an approach in which the frequency dependence of σ can be fitted according to the Almond-West type power law with a single exponent:

$$\sigma = \sigma_{DC} + A\omega^s, \quad (1)$$

where σ_{DC} stands for the DC conductivity and $A\omega^s$ is the AC contribution. It is evident from Fig. 4a and 4b that the DC conductivity σ_{DC} coincides with conductivity at 129 Hz in annealed samples (3b) and in untreated sample (3a) at higher temperatures. In the untreated sample the low frequency dielectric dispersion (below 1 kHz), mentioned above as Maxwell-Wagner relaxation, is strongly temperature-dependent. The Maxwell-Wagner relaxation can be described by Cole-Cole formula [13]:

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (i\omega\tau_{CC})^{1-\alpha}}, \quad (2)$$

where $0 \leq \alpha \leq 1$ are the parameters of width of Cole-Cole distributions functions, τ_{CC} is the mean and most probable Cole-Cole relaxation time, $\Delta\epsilon$ is the dielectric strength, ϵ_∞ is the high frequency dielectric permittivity. However, in our case the Cole-Cole fit for low frequency dielectric

dispersion cannot be performed, because the mean relaxation τ_{CC} is very long and $1/\tau_{CC}$ is substantially below of our low frequency limit. Nevertheless, it is easy to conclude that the mean relaxation τ_{CC} decreases on cooling in both annealed and untreated sample. In the Maxwell-Wagner relaxation case, $\tau_{CC}=RC$, where R and C is the resistance and the capacitance of grains, respectively. The capacitance of OLC aggregate, a sphere with radius r, can be described as $C=4\pi\epsilon_0r$. Therefore, the decrease of the mean Cole-Cole relaxation time τ_{CC} is related to the decrease of the mean size (radius) of the OLC aggregate.

From the Almond-West type fit it is possible to calculate critical frequency f_c , at which $\sigma(\omega)$ deviates from the dc plateau. Experimental value for f_c , have been defined as the frequency at which the value of conductivity is 10% higher than the DC conductivity value. The results are plotted in Fig. 5. As can be seen, the critical frequency value f_c of untreated samples (2a and 3a) at room temperature is very low, and falls below low frequency limit (20 Hz) of the equipment used. On heating above 350 K, the critical frequency for these samples strongly increases, but still remains lower in comparison with annealed samples.

To estimate an activation energy the temperature dependence of σ at 129 Hz (DC conductivity) for different OLC samples are presented in Fig. 5. The activation energy E of the conductivity and the conductivity prefactor σ_0 was evaluated using the Arrhenius law:

$$\sigma_{DC} = \frac{\sigma_0}{T} e^{-\frac{E}{kT}}. \quad (3)$$

The obtained parameters are listed in Table 2. It is evident that the activation energy E of the DC conductivity is higher in untreated samples and pure PU than that in annealed samples. The physics behind that can be associated with an electrical transport via electron diffusion through conducting OLC aggregates and (or) tunneling through a nonconductive (at low temperature) polyurethane matrix. The DC conductivity is a result mainly of electron tunneling through nonconductive polyurethane matrix, because no continued network of OLC clusters is observed in the composite (Fig. 1). Knowing that the activation energy E is a potential barrier for the carriers tunneling, it is reasonable that it is lower in more homogeneously annealed samples (Table 2).

The average time τ_n , which a charge carrier needs to travel through the OLC aggregate, is directly proportional to the aggregate size d . The biggest OLC size is observed in an untreated sample (Fig. 1), therefore, it is reasonable to assume that:

$$f_c \propto \frac{1}{\tau_n}. \quad (4)$$

For frequencies $f < f_c$ charge carriers can travel over different OLC aggregates within one electromagnetic wave period. In contrast, for frequencies above f_c the charge carriers can move mainly within a length of one OLC aggregate. Therefore, the critical frequency f_c and its temperature dependence reflect the mean OLC aggregate size. Hence, the observed increase in critical frequency f_c above 350 K manifests that OLC aggregate size is decreased. It can be thus concluded that annealing is a very important treatment for obtaining a homogeneous composite.

It deserves to emphasize that in contrast to heating measurements the temperature dependence of electrical conductivity and dielectric permittivity of both annealed and untreated samples on cooling is very weak (Fig. 6). Pronounced discontinuity between electrical conductivity and dielectric permittivity data on heating and on cooling indicate that the main composite homogenization process happens during isothermal annealing at 450 K. This temperature is close to the melting point of pure polyurethane (melting temperature of pure polyurethane was

established in additional experiment and found to be 489 K). A small increase of electrical conductivity σ on cooling in an untreated sample (above temperature 400 K) and in an annealed sample obviously is caused by a positive temperature coefficient effect [14]. The effect results from the break of the conductive links due to the thermal expansion of the polymer matrix. Some small decrease of dielectric permittivity ϵ' and electrical conductivity σ on cooling is observed in an untreated sample at low temperatures (below 400 K). This phenomenon is related to a negative temperature coefficient effect [14], which is caused by residual redistribution OLC aggregate in polymer matrix.

Finally, we have considered the frequency dependence of electrical conductivity σ on cooling. To analyze the data Eq. (1) was used. It was found that the critical frequency only slightly increases on cooling as it is seen from Fig. 7. The low-frequency dielectric dispersion (Maxwell-Wagner relaxation) is also almost stable on cooling. Therefore, one can note that the diffusion of OLC aggregates through polyurethane matrix mainly vanishes in cooling measurement and, as a result, a homogeneous composite is obtained.

4. Conclusion

The influence of a preparation procedure on dielectric properties of OLC-polyurethane composites was investigated. Two procedures were implemented: (i) mechanical stirring of OLC and PU in a solvent at increased temperature and (ii) annealing of the cured samples. It was concluded that heating of the suspension during mixing of OLC and PU has not so significant effect on the enhancement of the dielectric properties of the composites, as compared to an annealing of the cured sample. Samples annealed close to the melting point (450 K) exhibit substantially higher dielectric permittivity and electrical conductivity in comparison with an untreated sample. Dielectric permittivity, electric conductivity and critical frequency increased in the untreated sample during heating while Maxwell-Wagner mean relaxation time and average OLC aggregate size decreased. All parameters exhibited an offset close to the alpha (glass) transition temperature (380 K). Annealing of composites close to the melting temperature results in more homogeneous distribution of OLC. The temperature dependence of conductivity of a homogeneous sample is mainly caused by a weak positive temperature coefficient effect.

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List of Captions for figures and tables

Figure 1. SEM images of OLC/PU composites prepared under different conditions: untreated sample 3a (a) and sample 3b annealed at 150°C (b).

Figure 2. Frequency dependence of the real parts of complex dielectric permittivity ϵ' and complex electrical conductivity σ prepared under different conditions at room temperature.

Figure 3. Temperature dependence of the real parts of complex dielectric permittivity ϵ' and complex electrical conductivity σ of 3a (a) and 3b (b) sample on heating.

Figure 4. Frequency dependence of the real parts of complex dielectric permittivity ϵ' and complex electrical conductivity σ of 3a (a) and 3b (b) sample on heating.

Figure 5. Temperature dependence of conductivity at 129 Hz and critical frequency f_c on heating.

Figure 6. Temperature dependence of the real parts of complex dielectric permittivity ϵ' and complex electrical conductivity σ of 3a (a) and 3b (b) sample on cooling.

Figure 7. Temperature dependence of DC conductivity and critical frequency f_c on cooling.

Table 1. List of investigated OLC/PU composites.

Table 2. Parameters of Arrhenius law obtained from DC conductivity.

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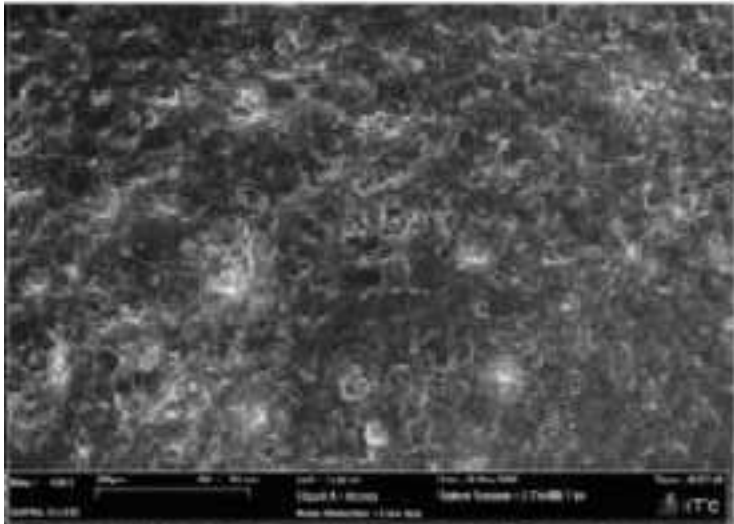
sample	OLC-PU mixing conditions	treatment of a cured sample
1a	1 day at 50 °C	untreated
1b	1 day at 50 °C	annealing at 150 °C
2a	1 day at 50 °C + 70 °C 2hr	untreated
2b	1 day at 50 °C + 70 °C 2hr	annealing at 150 °C
3a	1 day at 50 °C + 90 °C 2hr	untreated
3b	1 day at 50 °C + 90 °C 2hr	annealing at 150 °C

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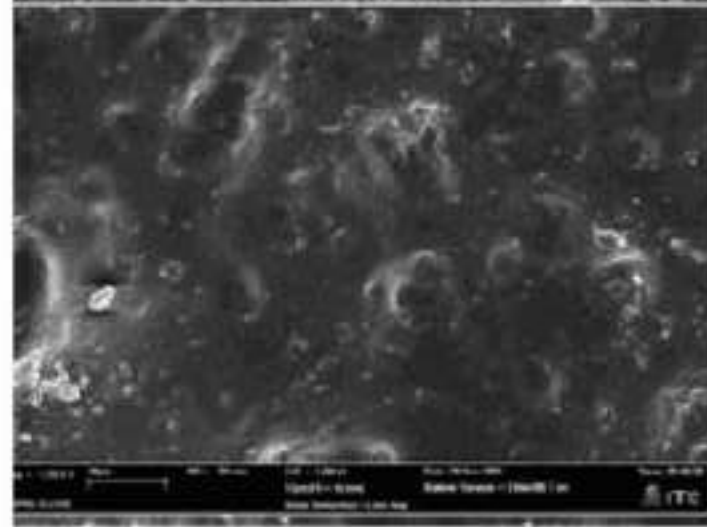
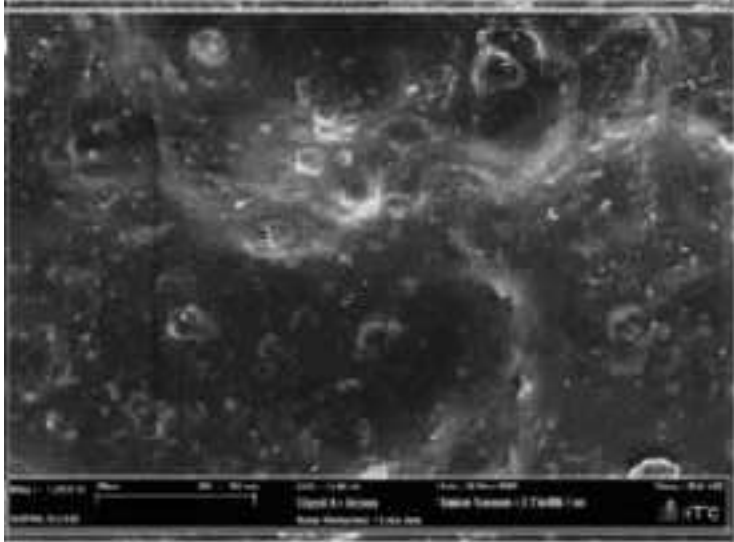
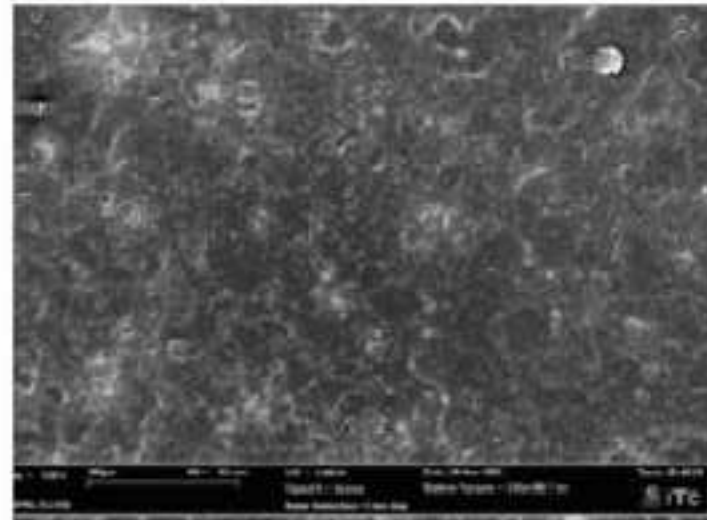
sample	$\ln\sigma_0$, S/m	E/k, K [eV]
1a	10.94	6485.2 [0.56]
1b	7.08	3668.2 [0.32]
2a	11.29	7400.4 [0.64]
2b	7.11	3466.4 [0.3]
3a	8.724	6086.6 [0.52]
3b	8.901	3377.2 [0.29]
pure polyurethane	5.94	7284.1 [0.63]

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